

Synthesis of an ionic liquid with an iron coordination cation†

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An iron-based ionic liquid, $\text{Fe}(\text{OHCH}_2\text{CH}_2)_2\text{NH}_6(\text{CF}_3\text{SO}_3)_3$, is synthesized in a single-step complexation reaction. Infrared and Raman data suggest $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$ primarily coordinates to $\text{Fe}(\text{III})$ through alcohol groups. The compound has T_g and T_d values of -64°C and 260°C , respectively. Cyclic voltammetry reveals quasi-reversible $\text{Fe}(\text{III})/\text{Fe}(\text{II})$ reduction waves.

Introduction

Room temperature ionic liquids (RTILs) containing transition metal elements are of both considerable intellectual interest and potential utility.¹ The high thermal stabilities and negligible vapor pressures of ionic liquids, coupled with potential value-added properties from transition metals, make them attractive for a wide range of applications.^{2–6} The conventional approach to form an ionic liquid is to employ a large, asymmetric organic cation with anions such as BF_4^- , PF_6^- , CF_3SO_3^- , or $(\text{CF}_3\text{SO}_2)_2\text{N}^-$.¹ Recently, a number of RTILs have been reported that contain transition metal-based anions. Examples include compounds containing imidazolium cations with tetrahedral halogenoferrates and phosphonium cations with various cobaltates as well as RTILs consisting of either alkyl ammonium, phosphonium, or imidazolium salts of polyoxotungstate clusters.^{4,5} There are also ionic liquids containing transition metal-based cations. Dai has reported RTILs that have $\text{Ag}(\text{H}_2\text{N}-\text{R})_2^+$ or $\text{Zn}(\text{H}_2\text{N}-\text{R})_4^{2+}$ (R = alkyl group) cations,⁶ and there are also a number of compounds containing ferrocenyl-functionalized cations.⁷ We now report the synthesis of $\text{Fe}(\text{OHCH}_2\text{CH}_2)_2\text{NH}_6(\text{CF}_3\text{SO}_3)_3$ (**1**), a viscous dark red liquid (at 25°C) containing an iron coordination cation. Complex **1** is characterized by elemental analysis, viscometry, TGA-DSC, infrared, Raman, and UV-Visible spectroscopy. The electrochemical properties of **1** are evaluated using cyclic voltammetry and impedance spectroscopy.

Results and discussion

The ionic liquid, $\text{Fe}(\text{OHCH}_2\text{CH}_2)_2\text{NH}_6(\text{CF}_3\text{SO}_3)_3$ (**1**), is obtained by mixing the solid metal salt $\text{Fe}(\text{CF}_3\text{SO}_3)_3$ with liquid $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$ in a 1 : 6 stoichiometry. The reaction is exothermic but additional heating is required to drive it to completion. A color change from almost white to red–orange is observed upon coordination of $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$ (Fig. 1a, inset). Conceptually, the synthetic method is similar to Dai⁶ in that an ionic liquid is produced through a complexation reaction of a metal cation with

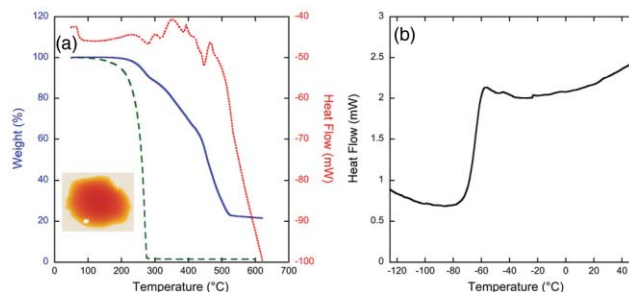


Fig. 1 (a) Photograph of **1** (inset) and TGA-DSC of **1**, (b) DSC of **1** with liquid N_2 quench cooling. The weight change and heat flow for **1** are illustrated as a solid blue line and a dotted red line, respectively. The weight change data for $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$ is represented by a dashed green line.

a neutral organic ligand, but there are two distinguishing features. First, this is not a metathesis reaction generating a secondary product that is isolated and discarded. Second, the presence of two simultaneously present functional groups (alcohol and amine) is required (assuming no change in hydrocarbon chain length). Reaction of $\text{Fe}(\text{CF}_3\text{SO}_3)_3$ with either $\text{CH}_2\text{CH}_2\text{NH}_2$ or $\text{CH}_2\text{CH}_2\text{OH}$ alone failed to produce an ionic liquid.

The stability of **1** was evaluated by thermogravimetric analysis (TGA) coupled with differential scanning calorimetry (DSC) and the results are shown in Fig. 1a. No change in mass is observed up to 260°C . Under identical conditions, $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$ alone starts to evaporate around 200°C . This observation provides evidence that (1) $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$ is coordinated to $\text{Fe}(\text{III})$ and that (2) $\text{Fe}(\text{CF}_3\text{SO}_3)_3$ is not simply dissolved in $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$ solvent.† A DSC measurement of **1** was also performed using a liquid N_2 quench cooling accessory and the results are shown in Fig. 1b. There is a T_g at -64°C that is indicative of an amorphous glass reforming a liquid upon heating.⁸

The infrared spectrum of **1** is shown in Fig. 2a. The infrared bands from $3500\text{--}3200\text{ cm}^{-1}$ and $3100\text{--}2700\text{ cm}^{-1}$ are associated with the alcohol and amine functional groups of $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$, respectively.⁹ The alcohol and amine bands of **1** are blue-shifted by approximately 200 cm^{-1} and 30 cm^{-1} , respectively, relative to $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$. The observed blue-shifts support the TGA data that indicate $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$ is coordinated to $\text{Fe}(\text{III})$. In addition, the larger blue-shift of the alcohol group relative to the amine indicates that $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$ preferentially coordinates through the alcohol groups.

The Raman spectra (633 nm laser) of $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$, **1**, and $\text{Fe}(\text{CF}_3\text{SO}_3)_3$ are shown in Fig. 2b. The $\text{Fe}(\text{CF}_3\text{SO}_3)_3$ symmetrical deformation and stretching frequencies associated with CF_3 (780 cm^{-1}) and SO_3 (1075 cm^{-1}) respectively, are red-shifted in **1**.⁹ This is consistent with displacement of CF_3SO_3^- by $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$ around the $\text{Fe}(\text{III})$ centers. In addition, there is a peak in **1** around 300 cm^{-1} not associated with either CF_3SO_3^- or $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$. This peak is associated with a $\text{Fe}\text{--}\text{O}$ bond

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† Electronic supplementary information (ESI) available: table of infrared data and viscosity data of **1**. See DOI: 10.1039/c0dt00523a

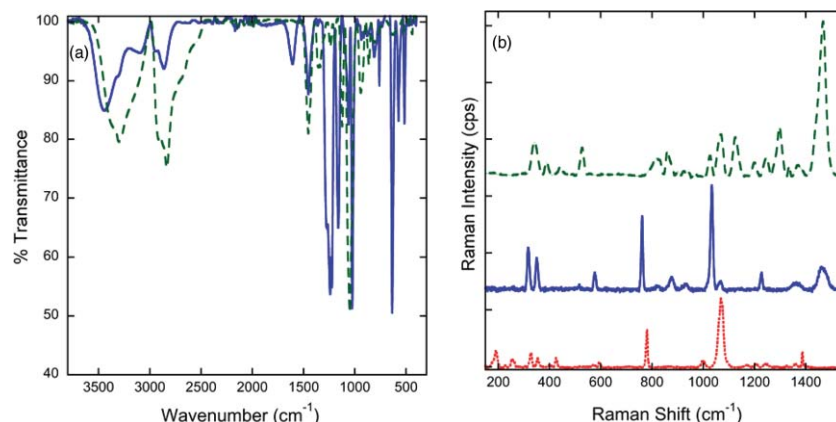


Fig. 2 (a) Infrared spectra of **1** (solid blue line) and $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$ (dashed green line), (b) Raman spectra (633 nm laser) of $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$ (dashed green line), **1** (solid blue line), and $\text{Fe}(\text{CF}_3\text{SO}_3)_3$ (dotted red line).

due to preferential coordination through the alcohol group of $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$.⁹

The high optical absorption of **1** prevented the direct acquisition of UV-Vis spectroscopic data. As a result, **1** was dissolved in 1-butyl-3-methyl-imidazolium hexafluoro phosphate (BMI-PF_6). A single λ_{max} was observed at 477 nm (Fig. 3a). The position of the λ_{max} at 477 nm, along with value of the extinction coefficient ($\epsilon = 63$), suggest this peak may be attributed to an iron $d-d$ transition and is consistent with preferential coordination through the alcohol groups. There are no changes to the infrared and Raman difference spectra (subtraction of solvent peaks) of **1** in BMI-PF_6 , and there is no shift in λ_{max} as a function of the concentration of **1**, suggesting that PF_6^- is not coordinating to $\text{Fe}(\text{III})$.

The specific conductivity of **1** (with < 2 ppm H_2O) at 25°C is $207\ \mu\text{S cm}^{-1}$. Although this value is similar to a number of conventional ionic liquids,² it is three orders of magnitude lower than traditional aqueous battery electrolytes such as H_2SO_4 and KOH .¹⁰ The low conductivity of **1** is consistent with the fact that it is highly viscous (4482 cP, see ESI for more information†). The activation energy of conduction, measured from an Arrhenius plot, is $13.1\ \text{kcal mol}^{-1}$. Typical activation energy values for conduction in aqueous and molten metal salts are $\sim 3\text{--}5\ \text{kcal mol}^{-1}$.¹⁰

The data suggests significant ion pairing is present in **1**. In contrast, the conductivity values reported by Dai for the $\text{Ag}(\text{H}_2\text{N-R})_2^+ / (\text{CF}_3\text{SO}_2)_2\text{N}^-$ RTILs range from $1.70\text{--}12.30\ \text{mS cm}^{-1}$ at 24°C .⁶ Although the higher charge of $\text{Fe}(\text{III})$ versus $\text{Ag}(\text{I})$ is an important factor, the results indicate that higher conductivity might be achieved by replacing the CF_3SO_3^- anion of **1** with the more hydrophobic $(\text{CF}_3\text{SO}_2)_2\text{N}^-$.

Cyclic voltammograms (CVs) of **1**, performed with a glassy carbon working electrode at four different scan rates, are illustrated in Fig. 3b. The high viscosity and low conductivity of **1** prevented the direct acquisition of electrochemical data. As a result, CV measurements were performed on a $0.011\ \text{M}$ solution of **1** in BMI-PF_6 , and stability was confirmed by UV-Vis measurements. Complex **1** displays several quasi-reversible waves associated with $\text{Fe}(\text{III})/\text{Fe}(\text{II})$ reduction and oxidation that become more resolved at slower scan rates. To further resolve these peaks, an Osteryoung square wave voltammogram was acquired on **1** (Fig. 3b, inset). The results show there are three waves. One plausible explanation for this behavior is the pendant $-\text{CH}_2\text{CH}_2\text{OH}$ groups of the $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$ ligands are coordinating to adjacent $\text{Fe}(\text{III})$ centers. This is consistent with the fact that the magnetic susceptibility measurement of **1** at 25°C shows there is a small amount of antiferromagnetic coupling (measured $\mu_{\text{eff}} = 5.78\ \text{BM}$ at

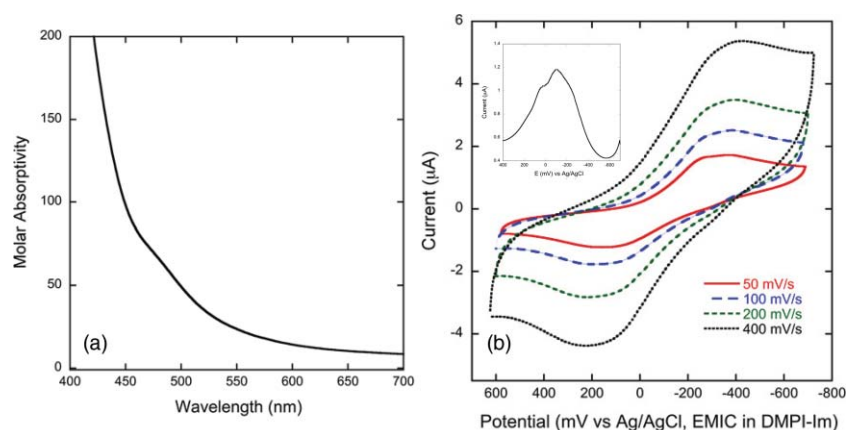


Fig. 3 (a) UV-Vis of **1** in BMI-PF_6 , (b) Cyclic voltammograms of **1** in BMI-PF_6 at four different scan rates ($50\text{--}400\ \text{mV s}^{-1}$) with a glassy carbon working electrode, (inset) Osteryoung square wave voltammogram of **1** (1 mV steps, sweep width amplitude 25 mV, sweep width frequency 15 Hz).

295 K; calculated 5.90 BM). In addition, there are several literature reports of magnetic interactions in transition metal-based ionic liquids.⁴

Conclusions

An ionic liquid containing an Fe(III) coordination cation is prepared by the reaction of $\text{Fe}(\text{CF}_3\text{SO}_3)_3$ and $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$. The compound is inexpensive to produce in high purity and has high thermal stability (up to 260 °C). Although the ionic conductivity of **1** is low, cyclic voltammograms indicate the compound displays quasi-reversible Fe(III)/Fe(II) reduction and oxidation waves and therefore may be described as a new type of liquid electrode.[§]

Experimental

General methods and materials

$\text{Fe}(\text{CF}_3\text{SO}_3)_3$ and $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$ were purchased from Aldrich. The $\text{Fe}(\text{CF}_3\text{SO}_3)_3$ was recrystallized from hot CH_3CN . Magnetic susceptibility measurements were made on a Johnson and Matthey MK-1 balance and Pascal's constants were used to obtain a diamagnetic correction. Thermal analysis was measured with a Mettler Toledo TGA/DSC 1 (Ar flow) and a TA Instruments DSC 2010 (with a quench cooling accessory, N_2 flow) with 10 °C min^{-1} heating. Infrared spectra were recorded on a Thermo Nicolet 380 FT-IR equipped with a Smart Orbit (Diamond) ATR accessory. Raman data were acquired on a Thermo DXR with a 633 nm laser. The visible absorption spectra (400–700 nm) were collected on a Shimadzu UV-3600. X-ray fluorescence was performed with a Thermo ARL QUANT'X analyzer. Elemental analyses (C, H, N, F, Fe, and S) were performed by Galbraith Laboratories, Inc. Water content was measured on a Mettler Toledo DL32 Karl Fischer coulometer. Viscosity measurements were made on a Brookfield DV-E viscometer.

Electrochemical studies

Conductivity measurements were made using a Solartron 1255B frequency analyzer with a SI 1287 electrochemical potentiostat using a custom cell with ~5 mm in diameter Pt working and Pt counter electrodes in a cofacial arrangement. This cell had a cell constant of ~10, as determined by measuring a solution of known specific conductance. The sample was thermally equilibrated prior to measurement by placing the cell in an instrumented Tenney environmental chamber to control temperature. Cyclic voltammograms were collected using a BAS100B potentiostat in a three-electrode cell. The working electrode was freshly polished 3 mm diameter glassy carbon, Pt wire was the counter electrode, and the reference electrode was Ag/AgCl in 1-ethyl-3-methyl-imidazolium chloride (EMIC) in 1,2-dimethyl-3-propyl-imidazolium bis(trifluoromethylsulfonyl) imide (DMPI-Im). All measurements were performed in a glove box under Ar.

Synthesis procedure

A 2.00 g (3.98 mmol) sample of recrystallized $\text{Fe}(\text{CF}_3\text{SO}_3)_3$ was added to 2.51 g (23.9 mmol) of $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$ in a 20 mL glass vial, thoroughly mixed for several minutes, and then heated

to 115 °C in an oven for 15–20 min. Additional mixing was then performed by ultrasound for 5 min and the solution was again heated to 115 °C for 15–20 min (yield >99.9%). IR (ATR, 4000–500 cm^{-1}): 3440 (m), 3309 (sh), 3094 (w), 2938 (w), 2862 (m), 1608 (m), 1453 (m), 1273 (sh), 1240 (s), 1224 (s), 1161 (s), 1061 (s), 1024 (s), 811 (m), 760 (m), 635 (s), 574 (m), and 515 (m). Raman (1800–200 cm^{-1}): 1464 (m), 1227 (w), 1033 (s), 878 (w), 817 (w), 761 (s), 577 (m), 517 (w), 351 (m), and 317 (m). Electronic spectral data (400–700 nm, in BMI-PF_6) [λ , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 477 (63). Density: $1.44 \pm 0.06 \text{ g mL}^{-1}$. Magnetic susceptibility: $\mu_{\text{eff}} = 5.78 \text{ BM}$ at 295 K. Anal Calcd (%) for $\text{Fe}(\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2)_6(\text{CF}_3\text{SO}_3)_3$: C, 28.6; H, 5.87; N, 7.41; F, 15.1; Fe, 4.9; S, 8.5. Found: C, 28.0; H, 5.76; N, 7.33; F, 14.7; Fe, 5.0; S, 8.8. [MW = 1134 g mol^{-1}].

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Notes and references

‡ There are a series of exotherms from 260 °C to 350 °C that correspond to the loss of $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$ ligands and this is further corroborated by X-ray fluorescence (no change in the Fe:S ratio of a sample heated in an oven to 350 °C). The onset of CF_3SO_3^- decomposition is approximately 350 °C, and it is consistent with a decrease in the Fe:S ratio.

§ In order to understand if the isolation of **1** is fortuitous or if it is the first member of a new family of ionic liquids, we have examined the reaction of other metal salts (including $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ and $\text{Cu}(\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CO}_2)_2$) with both $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$ and $\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$ ligands. To date we have synthesized and characterized three additional liquid materials: $\text{Zn}(\text{NH}_2\text{CH}_2\text{CH}_2\text{OH})_6(\text{CF}_3\text{SO}_3)_2$ (**2**), $\text{Cu}(\text{NH}_2\text{CH}_2\text{CH}_2\text{OH})_6(\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CO}_2)_2$ (**3**), and $\text{Cu}(\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2)_6(\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CO}_2)_2$ (**4**). Electrochemical studies of these complexes are presently underway and the results will be reported in due course.

- (a) T. Welton, *Chem. Rev.*, 1999, **99**, 2071–2084; (b) P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772–3789.
- (a) K. R. Seddon, *J. Chem. Technol. Biotechnol.*, 1997, **68**, 351–356; (b) R. Sheldon, *Chem. Commun.*, 2001, 2399–2407; (c) H. Olivier-Bourbigou and L. Magna, *J. Mol. Catal. A: Chem.*, 2002, **182–183**, 419–437; (d) J. Dupont, R. F. de Souza and P. A. Z. Suarez, *Chem. Rev.*, 2002, **102**, 3667–3692; (e) J. H. Davis, Jr. and P. A. Fox, *Chem. Commun.*, 2003, 1209–1212; (f) Z. Ma, J. H. Yu and S. Dai, *Adv. Mater.*, 2010, **22**, 261–285.
- Deep eutectic solvents are another family of ionic liquids that can contain a transition metal element. For more information, see (a) A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and V. Tambyrajah, *Chem. Commun.*, 2003, 70–71; (b) A. P. Abbott, J. C. Barron, K. S. Ryder and D. Wilson, *Chem.–Eur. J.*, 2007, **13**, 6495–6501; (c) J. Gorke, F. Sreenc and R. Kazlauskas, *Biotechnol. Bioprocess Eng.*, 2010, **15**, 40–53.
- Examples include: (a) S. Hayashi and H. Hamaguchi, *Chem. Lett.*, 2004, **33**, 1590–1591; (b) R. E. Del Sesto, C. Corley, A. Robertson and J. S. Wilkes, *J. Organomet. Chem.*, 2005, **690**, 2536–2542; (c) Y. Yoshida, J. Fujii, K. Muroi, A. Otsuka, G. Saito, M. Takahashi and T. Yoko, *Synth. Met.*, 2005, **153**, 421–424; (d) Y. Yoshida, A. Otsuka, G. Saito, S. Natsume, E. Nishibori, M. Takata, M. Sakata, M. Takahashi and T. Yoko, *Bull. Chem. Soc. Jpn.*, 2005, **78**, 1921–1928; (e) S. Hayashi, S. Saha and H. Hamaguchi, *IEEE Trans. Magn.*, 2006, **42**, 12–14; (f) Y. Yoshida and G. Saito, *J. Mater. Chem.*, 2006, **16**, 1254–1262; (g) R. E. Del Sesto, T. M. McCleskey, A. K. Burrell, G. A. Baker, J. D.

- Thompson, B. L. Scott, J. S. Wilkes and P. Williams, *Chem. Commun.*, 2008, 447–449; (h) Y. Yoshida, H. Tanaka, G. Saito, L. Ouahab, H. Yoshida and N. Sato, *Inorg. Chem.*, 2009, **48**, 9989–9991.
- 5 (a) M.-H. Chiang, J. A. Dzielawa, M. L. Dietz and M. R. Antonio, *J. Electroanal. Chem.*, 2004, **567**, 77–84; (b) P. G. Rickert, M. R. Antonio, M. A. Firestone, K.-A. Kubatko, T. Szreder, J. F. Wishart and M. L. Dietz, *Dalton Trans.*, 2007, 529–531; (c) P. G. Rickert, M. R. Antonio, M. A. Firestone, K.-A. Kubatko, T. Szreder, J. F. Wishart and M. L. Dietz, *J. Phys. Chem. B*, 2007, **111**, 4685–4692; (d) D. Ortiz-Acosta, G. M. Purdy, B. Scott, B. L. Bennett, R. E. Muenchausen, E. A. McKigney, R. D. Gilbertson and R. E. Del Sesto, *ECS Trans.*, 2009, **16**, 171–180.
- 6 (a) J.-F. Huang, H. Luo and S. Dai, *J. Electrochem. Soc.*, 2006, **153**, J9–J13; (b) *US Pat.*, 0146849 A1, 2008.
- 7 Representative publications include: (a) Y. Gao, B. Twamley and J. M. Shreeve, *Inorg. Chem.*, 2004, **43**, 3406–3412; (b) R. Balasubramanian, W. Wang and R. W. Murray, *J. Am. Chem. Soc.*, 2006, **128**, 9994–9995.
- 8 C. P. Fredlake, J. M. Crosthwaite, D. G. Hert, S. N. V. K. Aki and J. F. Brennecke, *J. Chem. Eng. Data*, 2004, **49**, 954–964.
- 9 (a) G. A. Lawrance, *Chem. Rev.*, 1986, **86**, 17–33; (b) *Handbook of Raman Spectroscopy: From the Research Laboratory to the Process Line*, ed. I. R. Lewis and H. G. M. Edwards, Marcel Dekker, New York, 2001; (c) G. Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, John Wiley and Sons Ltd., West Sussex, 3rd edn, 2001; (d) K. Golcuk, A. Altun and M. Kumru, *J. Mol. Struct.*, 2003, **657**, 385–393; (e) S. J. Angus-Dunne, L. E. P. Lee Chin, R. C. Burns and G. A. Lawrance, *Transition Met. Chem.*, 2006, **31**, 268–275; (f) C. M. Burba, N. M. Rocher and R. Frech, *J. Phys. Chem. B*, 2009, **113**, 11453–11458; (g) G. Litt and C. Almquist, *Appl. Catal., B*, 2009, **90**, 10–17.
- 10 *Handbook of Batteries*, ed. D. Linden and T. B. Reddy, McGraw-Hill, New York, 3rd edn, 2002.